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Effect of quasicrystalline phase on improving the corrosion resistance of a duplex structured Mg–Li alloy

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The in situ formation of I-phase improves the corrosion resistance of the duplex structured Mg–6% Li alloy. Corrosion attack on the surfaces of Mg–6% Li alloy is very inhomogeneous and severe pits and filiform corrosion clearly occur on the surfaces after immersion in 0.1 M NaCl solution. For the I-phase-containing Mg–6% Li–6% Zn–1.2% Y alloy, the corrosion attack is homogeneous and no severe pits and filiform corrosion can be observed.

Keywords: Mg–Li; Duplex structure; I-phase pockets; Pitting; Filiform corrosion

Due to the addition of lithium, Mg–Li alloys are the lightest metallic materials. Generally, their density is between 1.25 and 1.65 g cm^{-3}, which is about 1/2 and 3/4 that of Al and Mg alloys, respectively. Moreover, Mg–Li alloys can have attractive properties—such as high specific strength and elastic modulus, better formability, weak mechanical anisotropy and better mechanical properties at low temperature, etc. [1–2]—which have attracted great interest in the aerospace industry and for military applications [3–5]. However, Li is more active than Mg [6]. Alloying with Li can further degrade the corrosion resistance of the Mg substrate [6,7]. Song et al. indicated that the lower corrosion resistance of Mg–Li alloys compared to pure Mg is ascribed to their susceptibility to localized corrosion at the α-Mg/β-Li interfaces [7]. Recently, researchers found that I-phase (Mg_3Zn_6Y) could effectively improve the mechanical and corrosion properties of Mg alloys [8–23]. In the Mg–Zn–Y system, the corrosion rate of alloys with I-phase as the main second phase can be 10 times lower than that of alloys containing lower levels of I-phase [22]. Xu et al. reported that the formation ability of I-phase is very strong and mainly depends on the Zn/Y ratio of Mg alloys [12–14,19–20]. By controlling the Zn/Y (wt.%) ratio to be 6, I-phase can be formed in Mg–Li alloys [19,20]. Therefore, it can be predicted that the in situ formed I-phase c be helpful for improving the corrosion resistance of Mg alloys. However, previous work has mainly focused on the effect of I-phase on the corrosion resistance of Mg alloys containing no Li. In duplex Mg–Li alloys, the β-Li phase is more active than α-Mg matrix [7]. Moreover, the α-Mg matrix contains a certain amount of Li atoms. For these reasons, the corrosion resistance of Mg–Li alloys is commonly worse than that of Mg alloys that do not contain Li [6]. Thus, it is of great scientific interest to investigate whether the corrosion resistance of duplex structured Mg–Li alloys can be improved by I-phase formation. A study on this topic might offer a novel way for developing highly corrosion-resistant Mg–Li alloys, and also greatly deepen our understanding of the corrosion performance of I-phase-containing Mg alloys. In this work, by investigating and comparing the corrosion resistance of as-cast duplex structured Mg–Li alloys both with and without I-phase, i.e. Mg–6% Li and Mg–6% Li–6% Zn–1.2% Y, the underlying mechanism of I-phase in improving the corrosion resistance of duplex structured Mg–Li alloy will be explained in more detail.

Materials used in this study were as-cast Mg–6% Li and Mg–6% Li–6% Zn–1.2% Y (wt.%) alloys. Phase analysis was determined by X-ray diffraction (XRD) with a D/Max 2400 diffractometer. Microstructures of samples were observed by optical microscopy (OM) and scanning electron microscopy (SEM; XL30-FEG-ESEM). To avoid corrosion attack during preparation,

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specimens were polished to a 1 μm finish with kerosene and cleaned afterwards with acetone.

Potentiodynamic polarization experiments were carried out at a scan rate of 1 mV s^{-1} after the cell was held at the open-circuit potential (OCP) for 300 s using an EG&G potentiostat model 273 and a classical three-electrode cell with a Pt counterelectrode and saturated calomel reference electrode. Specimens were mounted using epoxy resin, leaving an exposed area of 1 cm^2. The measurements were performed in a 0.1 M NaCl solution at 25 °C. Using the same setup, electrochemical impedance spectroscopy (EIS) measurements were executed over a frequency range of 100 kHz to 10 mHz with 10 mV of amplitude of sinusoidal potential signals with respect to the OCP. The initial retard of 300 s was set to obtain a stable testing system. All electrochemical tests were repeated at least in triplicate. Samples 20 mm × 20 mm × 5 mm were immersed in 0.1 M NaCl for 7 days and cleaned in a hot chromic acid bath consisting of 180 g l^{-1} CrO_3 [7].

Due to the very low atomic number of Li, EDX cannot detect the existence of β-Li phase in the alloys. It has been reported that phases having higher atomic mass elements appear brighter on a backscattered electron (BSE) image [24]. Therefore, to distinguish α phase from β phase and determine their spatial arrangement, the BSE imaging mode is preferred. Figure 1 shows BSE images of two alloys. It can be seen that in the as-cast Mg–6% Li alloy, an obviously duplex microstructure, i.e. α-Mg + β-Li, is formed and the α-Mg matrix and β-Li phase exist in grey and dark, respectively (Fig. 1a). After the addition of Zn and Y, besides β-Li and α-Mg phases, obviously eutectic pockets and finely dispersed particles are formed in the Mg–6% Li–6% Zn–1.2% Y alloy (Fig. 1b). Moreover, compared with Mg–06% Li alloy, a larger amount of β-Li phase is formed and distributed more continuously in the Mg–6% Li–6% Zn–1.2% Y alloy. Previous work demonstrates that the formation of bright phases is ascribed to the addition of Zn and Y [19,21]. It can be seen that bright eutectic pockets are mainly distributed at β-Li/α-Mg interfaces. XRD confirms that the main phases in the Mg–6% Li–6% Zn–1.2% Y alloy are α-Mg, β-Li, LiMgZn, I-phase and W-phase, as shown in Figure 1c. Meanwhile, the diffraction peaks corresponding to the W-phase are very weak. Therefore, the bright phase in the eutectic pockets is mainly the I-phase and only a very little of W-phase exists at some particular α/β phase interfaces. Following this, the main phases present in two alloys are labeled in Figure 1a and b. Moreover, due to the Zn addition, the tiny bright dispersed dots in β-Li phases and the α-Mg matrix of the duplex Mg-Li alloys are LiMgZn phase [19].

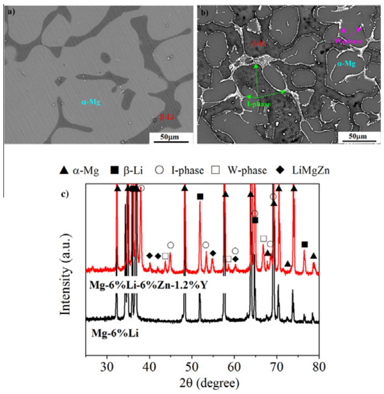

Figure 1. Microstructure of the as-cast alloys: (a) Mg–6% Li; (b) Mg–6% Li–6% Zn–1.2% Y. (c) X-ray diffraction patterns of the two alloys.

Figure 2a shows the polarization curves, indicating that the Mg–6% Li–6% Zn–1.2% Y alloy is more corrosion resistant than the Mg–6% Li alloy. This conclusion can be confirmed by EIS curves as the impedance of the Mg–6% Li–6% Zn–1.2% Y alloy is significantly larger than that of the Mg–6% Li alloy, as shown in Figure 2b. Another interesting observation is that low-frequency inductive loops can exist in the EIS curves of the two alloys, a finding that is mainly ascribed to the initial stage of the localized corrosion [7,25]. Figure 3 shows the corrosion morphologies of two alloys, demonstrating that the corrosion attacks on the two alloys are quite different. For the Mg–6% Li alloy, the corrosion attack on the surfaces is very inhomogeneous. Meanwhile, severely localized pits and filiform corrosion can occur on the surfaces, as shown in Figure 3a. However, for the I-phase-containing Mg–6% Li–6% Zn–1.2% Y alloy, the corrosion attack is homogeneous and no severe pits and filiform corrosion can be observed after the immersion, as shown in Figure 3b. A comparison of the corrosion morphologies further demonstrates that the in situ formation of I-phase can effectively improve the corrosion resistance of the duplex structured Mg–Li alloy. Cross-sectional observations to the immersed samples reveal that for the Mg–6% Li alloy, the corroded surfaces are mainly composed of the remaining β-Li phases and some eroded α-Mg matrix, as shown in Figure 3c. Since the corrosion resistance of I-phase is greatly superior [8,22–23], the I-phase pockets can be safely retained even after the immersion testing. For the Mg–6% Li–6%

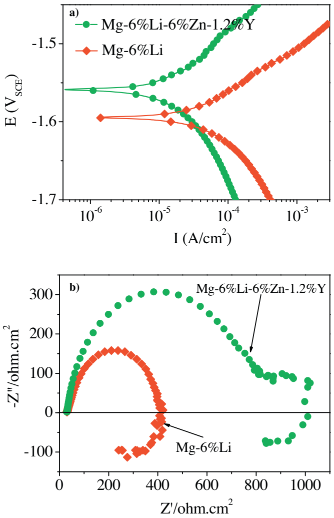

Figure 2. Electrochemically evaluated corrosion response measured in 0.1 M NaCl: (a) typical potentiodynamic polarization curves and (b) electrochemical impedance spectra of the as-cast Mg–6% Li and Mg–6% Li–6% Zn–1.2% Y alloys.